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Lead-Bearing Steels

THE successful production of free-cutting, open-hearth steels by the addition of about 0·2 per cent. of lead is not only a commercial development of great importance, but it raises questions as to the function of lead in bringing about ease of machining. An important paper* by representatives of the Battelle Memorial Institute and of the Inland Steel Company, Chicago, who originated the lead-bearing steel "Ledloy," not only gives extensive evidence for the improved machinability of the steels containing lead, but provides data which show that the lead is almost completely without effect on the mechanical properties at room temperature of carbon steels containing 0·15 to 0·5 per cent. of carbon in the normalised, cold-drawn, and oil-hardened and tempered conditions. It has very little effect on the impact figure at raised temperatures. It is also without appreciable influence on depth of carburising and on hardenability, but the lead-bearing steels have a slightly finer grain size and perhaps for this reason show slightly less depth hardening.

In view of the fact that lead is generally agreed to be almost, if not quite, insoluble in liquid and solid iron, and must therefore be liquid over a wide range of temperatures of working and treatment, these results are surprising. It is true that if the lead is allowed to segregate into microscopically distinct drops, which it may do if the amount added exceeds 0·5 per cent., cracking is experienced during rolling and the mechanical properties deteriorate. In commercial lead-bearing steels, however, containing under 0·25 per cent. of lead, no globules are visible under the microscope. The effect of lead on machining is additive to that of sulphur, but the properties of the high-sulphur, free-cutting steels are not affected in other respects by lead. In such steels some of the lead is contained in the inclusions as is shown by heating a polished section to 480 deg. Cent., after which lead globules are visible in the sulphide.

In speculations on the mechanism of the improvement in machinability brought about by lead, all the usual factors seem to be ruled out. Machinability can be improved by spheroidising the carbide, by coarsening the grain, by adding to the phosphorus or nitrogen content of the ferrite and so increasing its brittleness, by introducing non-metallic inclusions like sulphides, and by alloying additions which increase the rate of work hardening and so embrittle the chip. The effect of lead seems to fall into none of the above categories, and yet may be additive to the effects of any of these factors. Chips coming from the lead-bearing mild steels are observed to be at a lower temperature than those from lead-free mild steels machined under similar conditions. The former show a yellow temper colour when the latter are blue. This has suggested that the effect may be in the nature of lubrication produced by submicroscopic particles of lead.

That the lead exists as a fine dispersion of soft submicroscopic particles seems to be in accordance with the evidence put forward by the American authors. The dimensions of the α-iron lattice are unaffected, the lead-bearing steel is stained more than the lead-free steel by a solution of sodium picrate and sodium sulphide, but no particles are visible under the microscope. If this conclusion is correct, no analogous effect has been observed in fine dispersions of other elements and the influence on machinability of this type of structure seems to be specific to lead. Moreover, lead appears to be unique in producing ease of machining without sacrifice of any mechanical properties at ordinary temperatures and without introducing stress-raising inclusions into the steel.

* J. H. Nead, C. E. Sims, and O. E. Harder, "Properties of Some Free-machining, Lead-bearing Steels," *Metals and Alloys*, March and April, 1939, pages 68 and 109.

Silicon in Structural Steels

SILICON and silicon-manganese high-tensile structural steels have had a limited use in Great Britain and America. They have received wider application in Germany, where the steels used have usually been lower in carbon and higher in silicon content than in this country. It is generally agreed that in order to obtain the best results, the normalising or finishing temperature of a steel high in silicon should be higher than that of a similar steel low in silicon. In a paper by H. Wilhelm and J. Reschka[1] on the "Influence of Silicon in Structural Steels," the properties of a number of steels with carbon 0·17 to 0·5, silicon 0·01 to 1·3, and manganese 0·3 to 1·2 per cent. are recorded with special reference to the most suitable temperatures of normalising. The steels were investigated in the form of plates, 10 mm. and 50 mm. thick. Two compositions will serve as examples, viz.:—

C.	Si.	Mn.	S.	P.	Cu.
0·20	0·47	1·27	0·05	0·02	0·20
0·19	1·08	0·52	0·03	0·015	0·19

The first of these showed its best properties after it had been normalised from 880 deg. Cent. There was no substantial deterioration in properties until a normalising temperature of 930 deg. Cent. had been exceeded. It was necessary to normalise the second from 980 deg. Cent. to get the best results; the steel had a lower yield point in both the 10 mm. and the 50 mm. thickness, if a normalising temperature 20 deg.

lower was used. The mechanical properties after these treatments were as follows :—

	High Mn.	High Si.
Normalising temperature, deg. Cent.	880	980
Yield point, tons per square inch	25	24
Maximum load, tons per square inch	38	35
Yield ratio, per cent.	66	70
Elongation, per cent. on 200 mm.	20	21

Ageing after over-strain affects both types of steel similarly, as is illustrated by the results given in Fig. 1 for another two steels. A similar divergence in the normalising temperatures (880 deg. and 960 deg. Cent.) required to give the best properties in these steels is also to be observed.

The main object of Wilhelm and Reschka's paper is to draw attention to the high value of the upper limit of the critical range of high silicon steels. This is no new observation. It has long been known that the silicon-manganese spring steels require a specially high hardening temperature to ensure complete

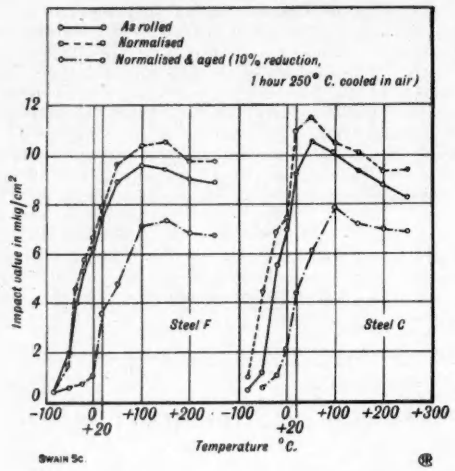

FIG. 1—*Notched-bar Impact Values of Steel F (C, 0·21 Si, 0·99; Mn, 0·48 per Cent. Normalised from 960 deg. Cent.), and Steel C (C, 0·21; Si, 0·43; Mn, 1·25 per Cent. Normalised from 880 deg. Cent.)*

hardening. Stainless steels high in silicon failed to respond to the standard heat treatment applied to those of the normal composition on account of the raising of Ac_3 by silicon and required an exceptionally high hardening temperature. F. Bonsmann[2] has recorded that cast silicon steels attain their best mechanical properties when they are annealed at a temperature 100 deg. to 150 deg. Cent. higher than that employed for plain carbon steels. It is well known from the study of the binary silicon-iron alloys that the A_3 point is raised rapidly by the addition of silicon to iron, a gamma loop being formed when the silicon reaches 2·5 per cent., according to P. Oberhoffer and C. Kreutzer,[3] or 1·85 per cent., according to F. Wever and P. Giani.[4] This involves a rise in Ac_3 of at least 40 deg. for 1 per cent. of silicon, Wever and Giani's figure being about twice as much as this. A widening of the gamma region occurs with the addition of carbon, and, according to E. Scheil,[5] at 0·32 per cent. of carbon a silicon content of 9·1 per cent. is required to close the loop. The rise of Ac_3 due to silicon is thus much slower in the presence of carbon, but is, nevertheless, definite. H. Buchholtz and E. H. Schulz[6] give the rise in the Ac_3 for silicon structural steels as equal to 50 deg. for each 1 per cent. of silicon. Wilhelm and Reschka have attempted to determine the critical range of nine steels by means of a dilatometer of simple construction. The dilatometer curves, of which an example is shown in Fig. 2, are somewhat difficult to interpret, but it appeared certain from microscopic examination of specimens quenched from various temperatures during heating that complete attainment of a uniform solid solution was not achieved until the temperature had risen beyond the kink in the heating curve, which is marked Ac'_3. On the assumption that this change in direction represented the upper limit of the critical range, Wilhelm and Reschka arrived at the following empirical formula for the end of the Ac point for silicon stee s of the compositions studied :—

$$Ac'_3\ (°\ C.) = 906 - 20\ (0{\cdot}1\ \text{per cent. C}) - 3\ (0{\cdot}1\ \text{per cent. Mn}) + 12\ (0{\cdot}1\ \text{per cent. Si}).$$

The calculated values for the high manganese and

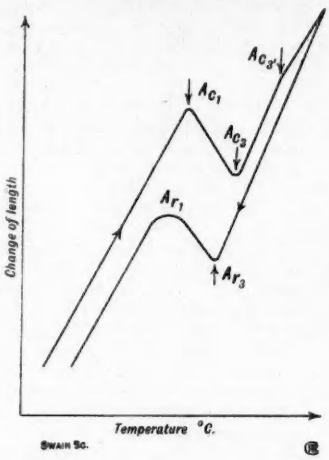

FIG. 2—*Dilatometer Curve of Silicon Steel*

high silicon compositions referred to above are 888 deg. and 982 deg. Cent. respectively.

A comparison of the temperatures given by this equation with those determined by Scheil and other investigators of the ternary iron-carbon-silicon system appears to indicate that the values now proposed are too high. On the other hand, the end of the critical range is not readily obtainable from ordinary thermal curves and silicon alloys are sluggish in attaining equilibrium, so that the formula of Wilhelm and Reschka may well be taken to give the most desirable temperature to use in practice as the finishing or normalising temperature of the high silicon structural steels.

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[5] See "The Alloys of Iron and Silicon," by E. S. Greiner, J. S. Marsh, and B. Stoughton, page 129.

[6] Werkstoff-Handbuch "Stahl und Eisen," V.D. Eisenhuttenleute, Düsseldorf, 1937, H. 41.

The Strain Age Embrittlement of Steel

By HUGH O'NEILL.*

IF a piece of ordinary mild steel as received from the hot rolling mill be cold worked by extension to 10 or 20 per cent. of its length, it is well known that tensile or hardness tests will reveal a certain amount of strain hardening. Furthermore, a notched bar impact test performed very soon after the straining will demonstrate that simultaneously the notch toughness has been reduced. If the strained steel is then rested for about a month, it will generally be found that a further spontaneous hardening has supervened, and the chances are that the impact value will have become still further reduced. The effect requires many days to be developed at room temperature, but it can be accelerated so as to occur in 30 min. by heating the metal to 250 deg. Cent. This peculiar change with time is known as the "strain ageing" of mild steel, and it was recently brought into prominence by two papers read in May before the Iron and Steel Institute. The title of one[1] referred to "strain-age-hardening" and was concerned only with tensile properties, whilst the second[2] adopted the title "Strain Ageing," and dealt with ductility and indentation hardness. In this connection it may be noticed[3] that an enterprising firm has actually utilised to advantage the increased *hardness* due to the ageing of cold-formed automobile wheel rims by reducing their section, which leads one to believe that the *embrittlement* which generally occurs is the most serious aspect of the whole curious business.

The phenomenon is somewhat of a metallurgical mystery and has quite properly become enshrouded in academic discussion. A few instances of failure encountered by the present writer may add a touch of reality, and at the same time may show the value of notch bar impact tests in relation to embrittlement effects.

As an introductory example a piece of mild steel, 1½in. thick, was recently being cold straightened before fitting into a carriage underframe. The required deformation, whilst very small, was sufficient to crack the member extensively and cause its rejection. It transpired that the plate was supplied with cold-sheared edges, and the evidence suggests that the strain due to shearing followed by the elapse of time before straightening had caused the development of strain age embrittlement. Other examples which have been examined more extensively are given with particulars in Table I, the test strain referring to an embrittlement test on the material involving about 15 per cent. elongation.

TABLE I.—*Brittle Failures Encountered in Practice together with Strain Ageing Test Results.*

Ref.	Specimen and observations.	Diamond hardness.			Izod impact test, ft.-lb.		
		Before straining.	After test strain.	Strained, and aged 30 min., 250 deg. C.	Before straining.	After test strain.	Strained, and aged 30 min., 250 deg. C.
1	Marine boiler plate—						
	Showed cracks round rivet holes of seams and cracks at bends :						
	(*a*) From flat,* as received	116	—	—	55	—	—
	From bend,* as received	165	—	—	15	—	—
	(*b*) From flat,* normalised	115	158	177	69	43	11
	Change...			+54%			−84%
2	Wagon strap bolt—						
	(⅞in. dia). cold bent and arc welded to frame ; broke off 1in. from weld :						
	(*a*) Unbent portion, as received	105					
	Region of fracture, as received	146					
	(*b*) From unbent portion	117	153	173	73	—	5
	Change...			+48%			−93%
3	Wagon underframe—						
	Of welded construction ; buckled by test collision, cut up by blow-pipe, and broke into pieces when straightened in press						
	(*a*) Unbroken portion...	143–157					
	Brittle region...	187					
	Normalised	135			22		
	(*b*) From unbuckled portion	143	187	209	15	—	7
	Change...			+46%			−53%

* Test piece in transverse direction.

The wagon underframe (specimen 3) of ¼in. section presents an interesting complication in that a temperature gradient due to flame cutting had been superimposed upon the strained metal before applying the static deformation which caused cracking. Further experiments were made to study the effect of this blow-piping, a preliminary test on the unstrained steel with a hardness of 148 showing that within ½in. of the flame cut edge a quench hardening up to 165 developed, but that no ageing changes were observable over sixteen days.

A tensile test piece with a 6in. parallel portion was then prepared and explored on one edge for uniformity of hardness. It was strained to 15 per cent elongation on 5in., and the parallel portion sawn longitudinally to give two similar pieces A and B. One of these A, was allowed to strain age naturally at room temperature, whilst a short piece was burned from the end of its neighbour B by means of the oxy-acetylene torch. Hardness explorations of both pieces were then made over a period of four-

* L.M.S. Research Laboratory, Derby.

teen days, with the results given in Table II.

By finally making impact test pieces from the two specimens A and B, it was shown that strain ageing had reduced the Izod value at least 53 per cent., whilst strain ageing and burning had reduced it 70 per cent. to 5 foot-pounds—a very low figure for mild steel. The impact values of the two pieces had changed more than the hardness values. It will be observed from Table II that the strain age hardening was greatest at about 1½in. from the burnt edge. This specimen C, however, has twice this impact value, although the hardness values are nearly as high as in specimen D. Once again hardness and toughness have not changed to the same degree. In general, it may be said that cutting under a stream of water has been beneficial, but, of course, the inherent properties of the steel have not been changed. Following upon these experiments it is obvious that the failure of the welded strap bolt (specimen 2) was facilitated by the thermal gradient due to the welding

TABLE II.—*Effects of Straining, Flame Cutting, and Ageing on Steel Ref. 3.*

	Specimen B : Burnt at one end after straining.					Specimen A unburnt.
Distance from burnt edge	½in.	1½in.	2½in.	3½in.	4½in.	
Before straining	147	142	145	142	142	143
Strained : 15 per cent. elongation	187	186	186	191	187	187
Aged 1 day	174*	210	206	198	191	190
Aged 4 days	174	214	206	198	198	196
Aged 14 days	171	214	208	206	202	209
Increase of diamond hardness by straining and ageing, per cent.	—	51	43	45	42	46
Izod impact value after ageing 20 days		5	5 = 5 ft.-lb.	5		8, 6, 6 = 7 ft.-lb.

* Partially softened due to flame.

indicates that the flame heating had not only increased the ageing, but had procured an optimum effect at this distance from the cut. An experiment was made on another piece of plate by burning off one end whilst a thermo-couple was inserted at 1½in. from the line of burning. In 30 sec. the temperature at this position had reached a steady maximum value of 205 deg. Cent. Such a temperature is known to accelerate the ageing effect and this probably explains why the underframe broke at a position about 1in. from the flame cut zone during straightening.

An experiment was made to see whether welded structures which have to be flame-cut could be spared the 200 deg. Cent. accentuated brittleness by cutting under water. A similar flat tensile piece as before was strained to 12 per cent. elongation on 5in., and cut longitudinally into two pieces C and D. The end was burnt off specimen C whilst being cooled with a stream of water, but D was burnt in air. The development of embrittlement may be seen from the figures in Table III.

Age hardening, as before, is at a maximum in a position about 1½in. from the burnt edge of the specimen D cut in air, and the Izod value has been reduced to 5 foot-pounds as before. The water-cooled

TABLE III.—*Effects of Flame Cutting Strained Steel Ref. 3 with and without Water Cooling.*

	Specimen C, water cooled.				Specimen D, air cooled.			
Distance from burnt edge	½in.	⅝in.	1½in.	2½in.	½in.	⅝in.	1½in.	2½in.
Unstrained	143	143	143	143	143	143	143	143
Strained, 12 per cent.—								
Aged 2 days	187	—	—	—	187	—	—	—
Aged 9 days	195	199	199	198	195	199	199	198
Flame cut—								
Aged 2 hours	193	205	201	198	160*	204	202	198
Aged 2 days	196	207	203	196	160	204	212	202
Increase of diamond hardness by straining and ageing, per cent.	—	45	42	37	—	43	48	42
Izod impact value, after ageing 7 days		10	8 = 10 ft.-lb.	12		4	7 = 5 ft.-lb.	4

* Partially softened by flame.

which followed the cold bending, but production difficulties with this detail have now been prevented by carrying out the bending at red heat. For purposes of information the composition and grain size of the specimens already mentioned are given in Table IV.

The purchaser of steel will naturally consider whether he can protect himself against being supplied with material which may be susceptible to strain age embrittlement. There is no doubt that the cause of the trouble lies in the steel-making process, for Krupps in 1926 pioneered the manufacture of "Izett," a non-ageing steel; whilst, on the other hand, certain basic open-hearth steels are very liable to the defect and the basic Bessemer process is perhaps the greatest potential offender. The application of the tensile strain ageing test to different steels is shown in Table V.

Alternative tests for strain ageing have been tried, such as making diamond pyramid indentations on the pre-strained bottom surfaces of 10mm. ball—1000kilo. load indents. The objection here is that the degree of strain produced by the Brinell ball cannot easily be made constant, so that strained and aged Izett gave an overall hardness increase of 38 per cent. whilst the

boiler plate specimen 1 increased only 28 per cent., their actual age-embrittlement tendencies having proved to be in the opposite order. Additional testing procedures are as follows :—

(*a*) Strain by bending a thin section in a vice, age at 250 deg. Cent., and test with a hammer (crude).

(*b*) Determine the tensile breaking strength with slow straining (*e.g.*, 20 min.) at 15 deg. Cent, and at 200 deg. Cent. If the latter value is much higher than the former the steel is liable to age embrittlement.

(*c*) The recovery of the yield horizontal in autographic tensile records of slightly strained specimens may provide a clue to ageing characteristics.

(*d*) Strained steels tested on the Föppl-Pertz damping tester show different damping curves, depending upon ageing properties.[5]

(*e*) The Erichsen test has usefully been employed in the L.M.S. laboratory to study changes of ductility following upon critical pre-straining in the Erichsen machine with subsequent ageing.[4]

On the whole, however, the critically strained tensile test piece from which notched bar specimens can be prepared provides the best means of studying ageing susceptibility.

Theoretical aspects of ageing merit some attention. The present writer is inclined to the view that oxygen or nitrogen or some related impurity is associated with the embrittlement. Schmidt[6] has indicted both oxygen and sulphur, and Whitely suspects the latter element. The evidence tends to show that increasing deoxidation of the liquid or solid steel reduces the strain-ageing effect. Experiments by Pfeil[7] demonstrated that no age hardening could be obtained with iron decarburised in hydrogen so as to contain less than 0·0025 per cent. C and very low oxygen, but by giving the same material an oxidising anneal the ageing effects returned. On the other hand, as regards "the possible influence of oxygen upon strain-age-hardening," Edwards and his collaborators[1] state that "all the evidence indicates that this element has no effect when the specimens are strained under pure tensile stresses and aged at temperatures of, say, 250 deg. to 300 deg. Cent.," and they prefer to direct attention to the yield point phenomenon. This is interesting, but the following paragraphs suggest grounds for believing that the yield effect and the "impurity" effect are actually related to each other.

When a piece of pure copper or aluminium is strained in tension, the load-extension curve proceeds smoothly from the origin to the point of fracture. Under the same conditions a piece of ordinary mild steel behaves differently, for a "yield" stress is reached at which an internal breakdown appears to occur in the metal. A horizontal step then develops in the load-extension diagram, and serrations are generally observed in autographic records of this step which correspond[8] with the facility for developing Fry etch bands on the surface. These etch bands only appear in certain steels and they have the configuration of Lüders' lines, and of the "stretcher-strains" which cause trouble in cold presswork.

The yield phenomenon appears to be due to a delayed plastic flow suggestive of the presence of an internal brittle scaffolding. The resistance of such a supposed structure permits straining to proceed up to the yield point at which the internal honeycomb (as Kuroda calls it) breaks down, whereupon the whole force is thrown on to the ductile ferrite crystals. Ludwik[10] in 1926 developed a theory to explain the yield point by considering that hydrogen and nitrogen became

TABLE IV.—*Chemical Analysis and Inherent Grain Size.*

Steel ref.	C.	Si.	Mn.	S.	P.	Cu.	Cr.	Ni.	McQuaid-Ehn test, A.S.T.M. No.
1	0·16	0·03	0·47	0·032	0·034	0·05	Trace	Trace	3–4 coarse
2	0·13	Trace	0·46	0·021	0·047	—	—	—	3 coarse
3	0·24	0·01	0·56	0·028	0·040	—	—	—	3 coarse
4	0·09	0·14	0·44	0·019	0·009	—	—	—	Fine
5	0·08	0·13	1·49	0·020	0·015	—	—	—	1 and 7 fine
6	0·20	0·12	0·59	0·023	0·023	—	—	1·83	—
7	0·15	0·07	0·67	0·027	0·034	0·04	—	—	3 coarse
8	0·165	0·05	0·66	0·035	0·042	—	—	—	—
9	0·18	0·02	0·56	0·036	0·025	Trace	—	—	3 coarse
10	0·02	Trace	0·08	0·03	0·03	—	—	—	Coarse

TABLE V.—*Strain Ageing Tests on Various Types of Steel.*

Ref.	Steel.	Diamond hardness.			Izod impact test, ft.-lb.		
		Before straining.	Strained.	Strained and aged.	Before straining.	Strained.	Strained and aged.
4	"Izett" steel	113	151	170 +50%	—	62*	65*
5	Drawgear steel, 1·5 per cent. Mn ...	142	179	189 +33%	117 unbroken	—	105 −10%
6	Acid 2 per cent. Ni plate	163	196	198 +21%	42	24	24 −43%
7	Acid boiler plate	150	163	179 +19%	32	—	19 −41%
8	Acid boiler plate	140	169	191 +36%	46	—	9·5 −79%
9	Basic boiler plate...	127	165	181 +42%	67	—	8 −88%
10	Basic conductor rail	89	135	148 +66%	19	5	2·5 −87%

* 10 mm. by 7 mm. test piece, owing to shortage of material, with notch in narrow edge.

dissolved in alpha iron and produced precipitation hardening effects. Kuntze and Sachs[11] supported this theory and decided that membranes of iron carbide provided the internal stiffening, whilst Kuroda[9] suggested carbide, nitride, other impurities, and a locally strained lattice as the constituents of his honeycomb.

Now Edwards, Jones, and Walters[1] believe that the holding up of continuous deformation in iron is due to the resistance at the crystal boundaries, and presumably their idea is that atomic disregistry at the boundaries produces the slip interference effects conceived by Jeffries and Archer. They therefore do not require that impurities be involved in the yield phenomenon, though why other metals besides iron should not similarly show yielding is not clear to the present writer. Proceeding further, they consider that ageing develops after yielding because the iron atoms at the boundaries "slowly acquire their original state relative to each other, but they do so at a much more accelerated rate on heating to 250 deg. Cent." Thicker grain boundaries are then supposed to build up, and these support the strain-hardened crystal cores, so that the steel acquires a renewed and increased yield point. The idea of a "recrystallisation" effect at the boundaries is not unreasonable, but confirmation is required that it occurs at the low temperatures under consideration, and the *occasional* embrittlement has still to be explained. Galibourg[12] has attributed strain ageing to the recrystallisation of amorphous metal formed on straining, and he considers the well-known blue brittleness around 250 deg. Cent. as being the same effect occurring instantaneously. The impurity theory, on the other hand, would suggest that during ageing, or at 250 deg. Cent., the impurity honeycomb is reconstituted and in a more dangerous form. Both theories could probably be accommodated to the fact[13] that the yield horizontal disappears when testing is carried out in the region 200 deg. to 300 deg. Cent.

It has been mentioned that Edwards and his collaborators[1] associate the yield effect with crystal boundaries, and necessarily require its absence in a single crystal. It is true that iron prepared by decarburising steel in hydrogen gives a vanishing yield horizontal as the grain size increases to the monocrystalline state.[14] On the other hand, Osmond and Frémont[15] reported a yield point in a large single crystal of iron produced by atmospheric decarburisation of a furnace buckstave. A large cast crystal of iron containing 1·8 per cent. Si examined by the writer[16] showed no well-defined yield point, and such an alloy is probably very low in oxygen content. What appears to be decisive evidence against Edwards is contained in the observation by Elam[17] that *single crystals* of aluminium containing 19 per cent. zinc, and having a close packed cubic atomic structure, show a definite yield point. This particular alloy is liable to contain oxide impurity and is considered by the present writer to support the view that the impurity structure even in single crystals is the cause of the yielding phenomenon.

Even if it were admitted that the yield effect and its associated ageing in iron depends chiefly upon crystal grain size there is a strong suggestion that grain size depends upon impurity. The decarburised iron and the silicon iron mentioned above are cases in point, and the various effects of hydrogen, phosphorus, oxidising conditions, and non-metallic inclusions upon the growth of large columnar crystals in steel may be recalled.[18] Houdremont and Schrader[19] consider that carbide, oxide, or nitride nuclei hinder grain growth in steel, and probably provide precipitation material for ageing effects. Bain[20] agrees with them that the addition of aluminium to produce fine-grained steel is effective because of the control of alumina nucleation—just as thoria controls the size of the crystals in a tungsten aggregate. Everything considered, the present writer does not believe that the work of Edwards, Jones, and Walters[1] weakens the theory that strain-age-embrittlement is due to oxygen or nitrogen impurity in some form or other. According to this theory, it follows that the steel maker must so control the charge, slag, temperature, and atmospheric conditions of his furnace that non-ageing steel shall be produced; whilst, on the other hand, the purchaser may have to decide whether appropriate acceptance tests shall be imposed where strain-age-embrittlement might lead to serious consequences in service.

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Temper-Hardening of Austenitic Steels Containing Boron

IT has been recognised since the publication of the investigations of F. Wever and A. Müller[1] on the iron-boron system that the pure iron-boron alloys are unlikely to respond to a temper-hardening treatment. Boron is soluble in γ-iron to the extent of about 0·15 per cent. at 1380 deg. Cent. The solubility falls to about 0·1 per cent. at the γ→α transformation temperature (915 deg. Cent.), and at this temperature the α modification will dissolve 0·15 per cent. The solubility of boron in α-iron falls slightly with falling temperature, being about 0·1 per cent. at 880 deg. Cent., and possibly 0·06 per cent. at atmospheric temperature. It was therefore realised that there was no chance of getting a supersaturated solution of boron by quenching from the γ condition, though there was some slight possibility of getting precipitation-hardening by a double treatment of the α solution. R. Wasmuth[2] experimented with the binary alloys without success, but he found that the austenitic chromium-nickel steels (carbon 0·15,

chromium 18, nickel 8 per cent.), containing 0·25 to 1 per cent. of boron, after being quenched from high temperatures, showed a considerable rise in hardness when reheated at 700 deg. to 800 deg. Cent. H. Bennek and P. Schafmeister[3] also carried out a considerable amount of work on the temper-hardening of austenitic chromium-nickel steels containing boron. Wasmuth attributed this temper-hardening to a modification of the solubility relations of boron in iron brought about by the presence of nickel and chromium. The true explanation was, however, never fully determined, and recently H. Cornelius[4] has investigated the behaviour of a number of chromium-nickel austenitic steels with a view to establishing more definitely the cause of the temper-hardening.

The iron-boron system, to which reference has already been made, contains the compounds Fe_2B (with 8·83 per cent. of boron) and FeB (with 16·23 per cent.). The nickel-boron system[5] contains Ni_2B (with 8·44 per cent. of boron), which is only very slightly, if at all, soluble in nickel at 1140 deg. Cent.

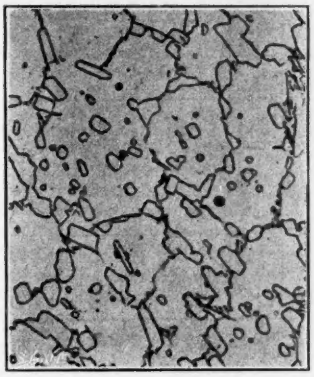

FIG. 1—*Alloy 2, Forged, Quenched from* 1200 *deg. Cent.*, × 500

Chromium[6] forms CrB (with 17·22 per cent. of boron) and manganese MnB; but their constitutional diagrams are not known, and neither is that of silicon-boron. The iron-boron-carbon system was investigated by R. Vogel and G. Tammann.[7] The γ solid solution was found to dissolve a maximum of 1·9 per cent. carbon with up to 0·3 per cent. of boron. The constituent in equilibrium with the γ solid solution was a solid solution of Fe_3C and Fe_2B containing up to 1·7 per cent. of boron and between 6·6 and 5·3 per cent. of carbon. The ternary pearlite consisted of Fe_2B (boron 8·83 per cent.), Fe_3C-Fe_2B solid solution (carbon 5·5, boron 1·4 per cent.), and α-iron-boron solid solution (boron 0·08 per cent.). This work revealed the probability that the presence of carbon was the most important factor in increasing the solubility of boron in steel at high temperatures.

Cornelius prepared a series of thirteen steels within the range of composition carbon 0·04 to 0·33, chromium 16·2 to 32·6, nickel 6·4 to 30·1, boron 0·8 to 1·7 per cent. They were made in 1-kilo. melts in a high-frequency furnace, the boron being added as 20 per cent. ferro-boron. The boron losses amounted to from 20 to 25 per cent. The steels were melted in magnesia crucibles and cast into iron moulds. All were forgeable at 1050–1150 deg. Cent., but great caution had to be exercised with the alloys containing 30 per cent. chromium and 15 per cent. nickel. The structure and hardness of the alloys were examined after a final reheating at 500–900 deg. Cent. after preliminary treatment at 1200 deg. Cent. for half an hour followed by air cooling or water cooling, or at 1000 deg. or 1100 deg. Cent. for one hour followed by quenching in water. Records of the change in length of the alloys when heated from atmospheric temperature to about 1000 deg. and cooled again were obtained on a Bollenrath dilatometer.[8] The results may be indicated briefly as follows:—

Cr 17 *Ni* 30 *B* 15 (1) *C* 0·04 (2) *C* 0·20.

In alloy 1 the hardness and structure were unaffected by any reheating treatment. In alloy 2 reheating had little effect after quenching from 1000 deg. Cent., but there was distinct hardening on reheating at 700 deg. after air cooling or water quenching from 1200 deg. Cent. The structures of the alloys 1 and 2 were similar, showing that addition of carbon does not lead to the formation of a new

FIG. 2—*Alloy 2, Forged, Quenched, and Tempered* 70 *Hours at* 800 *deg. Cent.*, × 500

constituent. It was therefore assumed that carbide enters the boride phase forming a carbide-boride solid solution (the *x*-phase), not soluble in the γ solid solution. The structure of alloy 1 was unaffected by reheating after quenching, but in alloy 2 the austenitic ground mass was darkened by heating at 700 deg. Cent., and showed distinct precipitation after seventy hours at 800 deg. Cent., a treatment which is associated with marked softening of the temper-hardened alloy (Figs. 1 and 2).

The dilatometer curve of alloy 2 shows that the precipitation of *x* above 730 deg. Cent. is accompanied by a slight progressive contraction. Although alloys 1 and 2 showed no α-iron, they were in all conditions of heat treatment fairly strongly ferro-magnetic.

Cr 30 *Ni* 15 *B* 1·6 (3) *C* 0·05 (4) *C* 0·23

The low-carbon alloy 3 showed no temper hardening. Alloy 4 showed an increase in hardness when heated at 700 deg. after being quenched at 1250 deg. Cent. The dilatometer curve of the quenched alloy showed a slight contraction between 700 deg. and 800 deg. Cent. Both alloys were non-magnetic in all conditions of heat treatment, and showed a structure of the *x*-phase in γ solid solution, the *x*-phase

being precipitated from γ in alloy 4 by suitable treatments.

Cr 16	*Ni* 15	(5) *B* 1·5	*C* 0·06
		(6) 0·9	0·27
		(7) 1·3	0·33

The low-carbon alloy 5 showed no change, while both carbon-rich alloys showed temper hardening when heated at 700 deg. after being quenched from 1200 deg. Cent. The increase in hardness was rather less than in alloy 2 with higher nickel, and greater than in alloy 4 with higher chromium. The dilatometer curve of alloy 5 showed uniform expansion and contraction, that of alloy 7 quenched from 1200 deg. in water showed a contraction between 700 deg. and 900 deg. Cent., with no further change on subsequent reheating (Fig. 3). This contraction was associated with the precipitation of the *x*-phase, which was visible in the coalesced condition in micrographs taken after heating for eighty hours, at 800 deg. Cent.

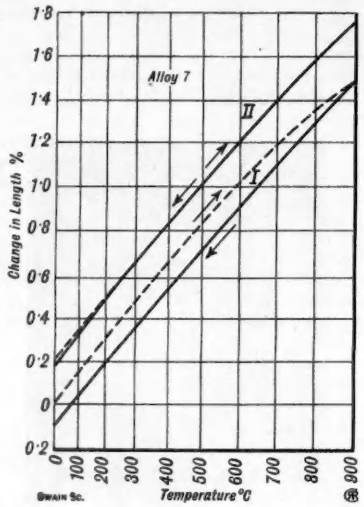

FIG. 3—*Dilatometer Curves, Alloy 7. I, Quenched in Water from 1200 deg. Cent.; II, After the Reheating given in I*

Cr 17 *Ni* 10 (8) *B* 0·8 *C* 0·18

There was a very slight increase of hardness of this alloy (8), as reheated at 700 deg. Cent. after being quenched from 1200 deg. Cent. Comparison of alloys 2, 6, and 7 with 8 shows that the increase in hardness falls off with decrease in nickel content. In the quenched condition, alloy 8 was slightly magnetic, and its magnetic properties were not appreciably altered in the temper-hardened state, so that it may be assumed that the alloy contained stable austenite. There was a contraction in the dilatometer curve at 700–800 deg. Cent. and the microstructure showed precipitation and balling up of the *x*-phase after eighty hours at 800 deg. Cent.

Cr 18	*Ni* 8	(9) *B* 1·4	*C* 0·06
		(10) 0·9	0·26
		(11) 1·5	0·25

The alloys of this (and of the next) group differ in important respects from those previously described. For example, alloy 9 showed temper hardening in spite of its low carbon content, and the amount of hardening was independent of the temperature of the preliminary quenching (provided that it exceeds 1000 deg. Cent.) and was the same after air cooling and water cooling. As quenched, the alloy was non-magnetic and austenitic in structure ; after tempering it was magnetic and martensitic. X-ray analysis showed no α in the quenched condition and no γ after reheating at 700–800 deg. Cent. After tempering, the α lines were much stronger than those of the *x*-phase. Thus the hardening of alloy 9 was not due to precipitation, but to the formation of martensite. Boron-free steels of composition similar to 9 consist of stable austenite, but by the formation of the borides Ni_2B and CrB the nickel and chromium content of the solid solution is lowered and the austenite rendered less stable. The dilatometer curve of alloy 9, quenched in water from 1200 deg. Cent. and reheated at 700 deg. Cent. (Fig. 4), shows a contraction at 530 deg. to 750 deg., due to the reversion to austenite of the martensite produced on tempering. The austenite of alloy 10, on account of its lower boron and higher carbon content, is more stable than that of 9 and hardening due to its decomposition was less pronounced. Its low nickel content also makes the precipitation which contributes to the hardening less effective than in alloys 2, 6, 7, and 8. The combined influence of martensite formation and precipitation in alloy 10 was confirmed by microstructure (Fig. 5), magnetic testing, and X-ray analysis. In alloy 11, on account of its higher boron content with the same relatively low nickel, the effect of austenite decomposition outweighs that of precipitation. Though in the quenched condition X-ray analysis shows the presence of the γ and *x*-phases, γ appears to be entirely replaced by α after the tempering treatment. This explanation of the hardening process is confirmed by dilatometer curves (Fig. 6). Curves I and *a* show the behaviour of the alloys as water quenched from 1200 deg. Cent. The contraction beginning at 700 deg. Cent. is due to the precipitation of the *x*-phase. The increase in length in the cooling curve is due to the formation of martensite. On reheating (curves II and *b*) the reversion of martensite to austenite begins at about 530 deg. Cent. and on cooling again the reverse process takes place below 100 deg. Cent.

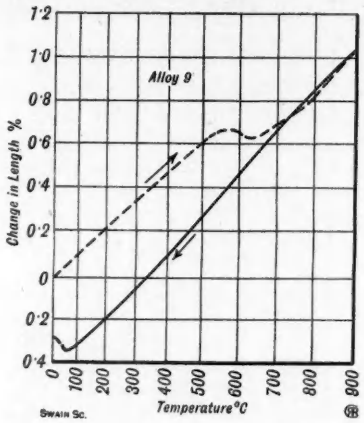

FIG. 4—*Dilatometer Curve, Alloy 9, Quenched in Water from 1200 deg. Cent., and heated 24 Hours at 700 deg. Cent.*

Cr 18 *Ni* 6 *B* 0·8 (12) *C* 0·04 (13) *C* 0·23

In alloy 12 the condition as quenched from 1200

deg. Cent. was mainly ferritic (δ-iron). Dilatometer curves showed no precipitation on heating, but a change to martensite on subsequent cooling. Alloy 13 had a pure austenite groundmass in the quenched condition, and showed its maximum hardness after

FIG. 5—*Alloy* 10, *Quenched and Reheated* 80 *Hours at* 800 *deg. Cent.*, × 500

being reheated to 900 deg. Cent. The dilatometer curves showed pronounced martensite formation, the microstructure showed darkening of the groundmass at 700 deg. Cent. coalescence at 800 deg. Cent. and both coalescence of bright particles and darkening of the groundmass at 900 deg. Cent. It appears that the maximum hardness induced by treatment at 900 deg. Cent. was due to the reduced stability of the

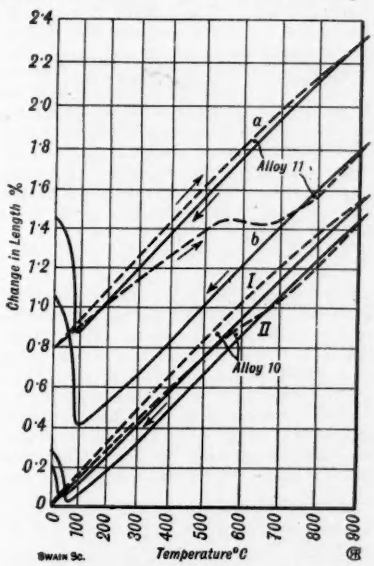

FIG. 6—*Dilatometer Curves, Alloys* 10 *and* 11

austenite brought about by increased precipitation and coalescence of borides.

CONCLUSIONS

The results of this work indicate that boron alloys of very low carbon content show no susceptibility to precipitation hardening; with higher carbon susceptibility to precipitation hardening is reduced by lowering the nickel or raising the chromium content. The precipitation is controlled by carbon content; the hardening constituent is a boride-carbide solid solution. Precipitation of this phase may have a direct hardening effect, but may also function by depriving the austenite of its stabilising elements, and so inducing transformation to martensite on slow cooling or reheating. The temper hardening of the low-carbon austenitic steels containing 8 per cent. or less of nickel is shown by Cornelius to be due solely to the formation of martensite, though when the carbon is higher the martensite formation may be preceded by a true precipitation hardening. Even so, however, the temper hardening by boron of the chromium nickel austenitic steels is held to be primarily due to martensite formation when the nickel does not exceed 8 per cent. Thus it may be concluded that Wasmuth's speculations on the effect of alloy elements on the solubility of boron in iron are unwarranted, and that the temper hardening observed by him in steels containing carbon 0·15, chromium 18, and nickel 8 per cent., together with boron up to 1 per cent., was mainly due to the formation of martensite.

In elucidating the mechanism of temper hardening produced by boron, Cornelius has made a useful contribution to the subject, and its possible bearing on the explanation of temper hardening of austenitic steels containing other elements (*e.g.*, beryllium) should not be overlooked.

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Researches on the Deep-Drawing Process

A COMPREHENSIVE study has recently been published by S. Fukui* on the mechanism of a simple drawing process for the pressing of cylindrical cups from flat circular blanks. By introducing a correcting term for the shoulder of the die, he was able to obtain a new relation between the punch load P, the blank holder force H, and the induced stresses, for a conical die, which was considered more satisfactory than existing relationships as found by Drs. Sommer and Sachs. This revealed that the punch load is dependent upon the drawing conditions, upon the angle of the conical die, and upon the distribution of thickness and circumferential stresses in the pressing. Since these latter are not known experimental measurement is essential.

Accordingly, a special apparatus was constructed, in which the drawing or punch load and the blank-holder load were measured by the piezo-electric effect on two quartz crystals. Three types of holding were used—rigid holding by rods, spring holding,

* S. Fukui, "Researches on the Deep-Drawing Process," Scientific Papers of the Institute of Physical and Chemical Research, Tokyo, October, 1938, 34, 1422–1527.

and "gummy" holding by inserting a rubber ring. The elastic movement of the latter two allows corresponding thickness changes in the blank to occur during drawing. The depth of draw was measured by the change in electrical capacity of a tube condenser.

Records of all three changes were taken simultaneously by combining three string electrometers so that the deflections of all three are focused on a single plate. Fig. 1 shows typical autographic records, the deflection of the string being ordinate and time the abscissa. Curve I gives the change in punch load P, rising to a maximum and falling gradually. Curve II shows the holding force H increas-

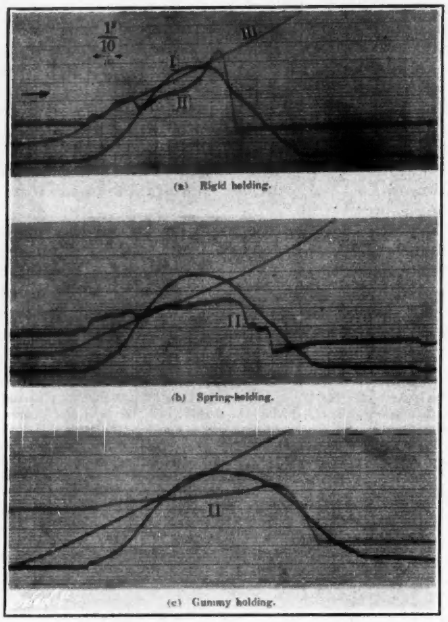


FIG. 1—*Experimental Records*

ing from its initial value to a maximum and falling suddenly as the flange of the partial pressing is drawn from beneath the holding pad. Curve III indicates the depth of draw h. The value of H is materially affected by the method of holding, there being a much smaller percentage change in gummy holding than with the other two types.

The materials selected for the work were Armco iron and aluminium (98·2 per cent.). Blanks from 29 mm. to 40 mm. diameter were lathe turned and subsequently annealed at 915 deg. and 350 deg. Cent. respectively; the press was constructed for a punch diameter of 18 mm. and was used mainly with rigid holding, the initial holding load being 28·5 kilos. The thickness of blank selected was 0·50 mm., chosen after experiments had shown that the punch load increased linearly with the thickness.

EXPERIMENTAL RESULTS

Effect of Radius of Die and of Punch Head.—For investigating the effect of punch radius in profile on the maximum punch load P_{max}, punches ranging in radius from 0·5 mm. to 9 mm. were used with both iron and aluminium blanks, other conditions being constant. No effect was found on P_{max} for increased punch radius, but the rising pressure curve on the diagram is more gentle and the working stroke is increased. The net effect on the total press work is negligible. Since the cups fracture at the radius between the base and the side cylindrical wall, the larger punch radii r_p enable larger blanks to be drawn (Table I), owing to the reduced amount of thinning at the radius at the base of the cup:

TABLE I.—*Deep Drawing of Armco Iron Blanks.*

Thickness of blank	t_o = 0·5 mm.
Diameter of punch	d_1 = 18·0 mm.
Diameter of hole in die	d_2 = 19·5 mm.
Radius of curvature of shoulder of die	r_d = 3·0 mm.
Radius of curvature of punch head	r_p } see below
Initial diameter of blank	D_o } see below
Maximum load just before fracture	P_z } see below

r_p, mm.	D_o, mm.	P_z, mm.
0·5	35	960
1·5	37	1110
2·5	38	1190
4·0	39	1200
6·0	39	1190
7·5	39	1220
9·0	39	1220

The punch load P_z increases with r_p and reaches a nearly constant value at about $r_p = 3·0$ mm., or $= 6\,t_o$. Similar tests with die radius from 1 mm. to 6 mm. showed that the punch load decreased as r_d increased. The main effect of increasing the die radius, apart from the fall in maximum load, was to make the rise and fall of the pressure curve more gradual and to maintain the high load for a shorter period of the stroke. This gives an economy in the total press work required to draw the cup. The maximum holding force also decreases with increase of die radius and is maintained over a shorter time. Experiments were made with increasing initial blank-holder loads. The effect was to increase both the maximum punch load and the holding force H_p at the instant of P_{max}. It is suggested, therefore, that for increasing die radii some part of the decrease in P_{max} may be attributed to the fact that the holding force is diminished and exists over a shorter period. Thus, in general, the punch load for any given blank diameter depends mainly upon the die radius whilst the punch curvature controls the maximum permissible punch load. We should therefore use generous die radii to give the minimum press work and maximum safety margin.

EFFECT OF SPEED

Over the range of testing, 2–10 mm. per second, the speed of draw was found to have little effect upon the autographic diagram. The punch load, P_{max}, increased slightly and the total energy also increased. The reason for this is that the plastic flow, in requiring time to develop, requires a greater force to be applied for a given strain, the more rapid the rate of straining. The results, however, agree with Sommer's conclusions in that no effect is found between the range 0·1–2 mm. per second for brass, copper, and aluminium.

EFFECT OF LUBRICANT

Investigations showed that there was little percentage gain by lubricating the ordinary surfaces. By thoroughly degreasing the blank, die, and holding pad by prolonged immersion in benzene, the author showed that the punch load required to draw a given blank with these conditions was greater by approximately 40 per cent. for iron and 75 per cent. for aluminium, respectively, compared with the ordinary state. Normal conditions therefore, in

which some measure of grease is present, do not show much change on P_{max}, by using additional lubricant.

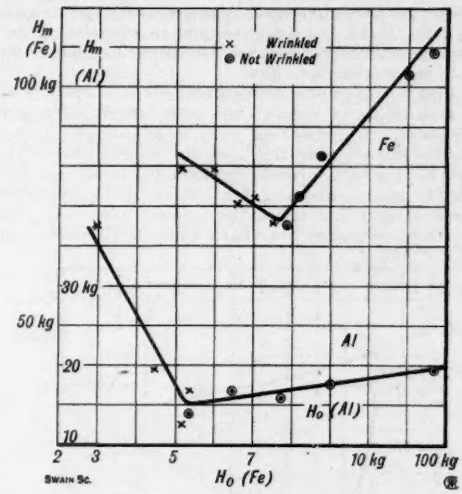
LIMITING HOLDING FORCE REQUIRED TO PREVENT WRINKLING

Since the effect of increased blank-holder load is to increase the punch load in roughly proportionate manner, it was felt desirable to reduce the initial holding force H_o to its minimum. The lower limit is determined by the limiting holding force H_n required to prevent wrinkling of the cup (Fig. 2). The existence of wrinkling is sensitively shown by the second maximum in the pressure curve, due to the height of the wrinkles, which form on the flange, being greater than the radial clearance. "Gummy" holding was employed for the tests since the change in holding force is not more than 20 per cent., so long as wrinkling is absent. When wrinkling occurs, however, the gum ring is compressed, holding up the pad, and the increase in H is recorded as in the figure. Curves of maximum holding force H_m plotted against the initial holding force H_o show a minimum value corresponding to the limiting holding force required to prevent wrinkling H_n (Fig. 3).

The tendency to wrinkle (and, consequently, the limiting holding force) decreased with increase of thickness of the blank, whilst a critical value was found for the radial clearance, where H_n rose suddenly for clearances less than 140 per cent. of the initial thickness, *i.e.*, 0·7 mm. clearance for blanks 0·5 mm. thick.

An examination of the effect of the radius of punch head, r_p, showed that the limiting holding force is little affected, decreasing only slightly with r_p. Since the critical wrinkling phase occurs during the later stages of the draw, when the metal in the neighbourhood of the punch head has almost completed its deformation, this is not surprising.

At this lower limit of blank-holder pressure the



(t_o=0·5, D_o=35·0, d_1=18·0, d_2=19·5, r_d=3·0 mm.)

FIG. 3—*Maximum Blank Holding Load H_m Plotted Against Initial Blank Holding Load H_o for Iron and Aluminium*

tendency for wrinkling increased considerably the sharper the die radius—that is, a greater limiting holding force was required to prevent the develop-

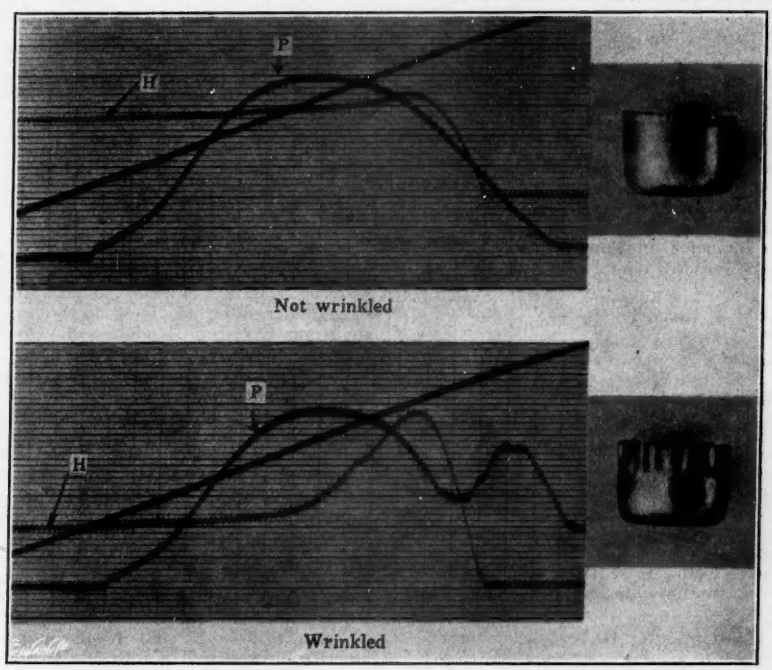
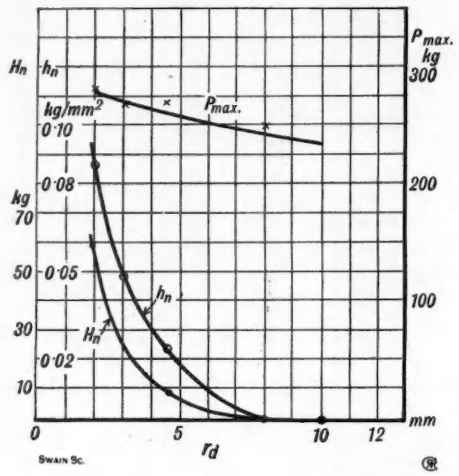


FIG. 2—*Effect of Blank Holding Load on Wrinkling*

ment of the wrinkles. Fig. 4 shows curves for aluminium and includes the limiting intensity of holding force h_n calculated on the initial flat holding area. It is seen that no holding force is required when the die radius reaches the limiting value, such that the blank diameter is equal to the sum of the die diameter, plus twice the die radius, *i.e.*, when the holding area becomes zero.

Under conditions of limiting blank-holder load, this limit is, of course, less with blanks of larger diameter. Investigating with iron and aluminium it was found that the limiting holding force H_n increased with the blank diameter D_o, in an approximately linear manner, for blanks with diameters greater than 1·9 times the punch diameter. The intensity of holding force h_n for iron is almost constant



(t_o=0·5, D_o=36·0, d_1=18·0, r_p=3·5, d_2=19·5 mm.)

FIG. 4—H_n, h_n *and* P_{max} *for Aluminium Plotted Against the Radius of Die* r_d

for such values of D_o, but increases linearly for aluminium. Curves are seen in Fig. 5. The author gives the limiting value for the intensity of holding force for various metals under conditions of thickness 0·5 mm., die diameter 19·5 mm., punch diameter 18 mm., and die radius 3·0 mm. as follows :—

	Kg./mm.².	Lb./in.².
Iron	0·16–0·18	(228–256)
Aluminium...	0·03–0·07	(43–100)
Copper	0·08–0·12	(114–170)
60/40 brass...	0·11–0·16	(157–228)

EFFECTIVE DRAWING FORCE

An approximately linear relationship existed between P_{max} and the blank diameter for iron. Since the punch load will be zero to draw a blank of diameter equal to the die diameter, the author suggested that the effective area of blank was the whole area less the area of the die hole. It was found that a linear relation held between this effective area and the maximum punch load. Since, then, P_{max} is zero for no effective area, we have the empirical relation that

$$P_{max}=p_{max} \cdot \frac{\pi}{4}(D_o^2-d_2^2),$$

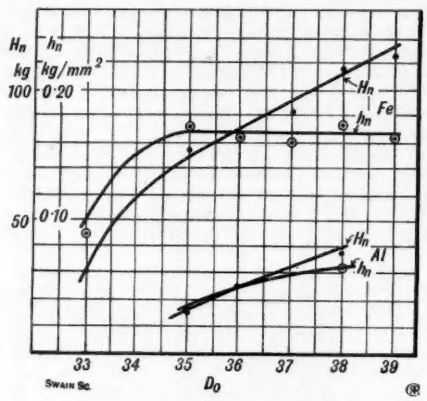
where p_{max} is the unit effective drawing force in kilogrammes per square millimetre. Similar results were obtained for aluminium, copper, and 60/40 brass. Typical values of p_{max} kilos. per square millimetre for blank thickness 0·5 mm., die diameter 19·5 mm., and die radius 3 mm. for gummy holding with limiting holding force are :—

	Kg./mm.².
Iron	1·32
Aluminium	0·384
Copper	0·852
60/40 brass	1·33

The value of the unit effective drawing force will obviously depend upon the conditions of drawing, such as the die or punch radius, the nature of the lubrication, and method of holding. Calculations of p_{max} from results by Sachs confirm the existence of an empirical relation, although the values differ somewhat owing to differences in experimental conditions.

STRENGTH OF DEEP DRAWING

As stated before, fracture of the cups generally occurs between the bottom radius and side cylindrical



(t_o=0·5, d=18·0, d_2=18·5, r_p=2·5 (Fe), 3·5 (Al), r_d=3·0 mm.)

FIG. 5—H_n *and* h_n *for Iron and Aluminium Plotted Against the Initial Diameter of Blank* D_o

wall. Failure will then occur when the stress transmitted by the wall exceeds the strength of the material. It is interesting to note here that the strength at failure, calculated on the original area for the larger punch radii, is considerably greater than the nominal strength of the material. This may be due to the metal having been subject to cold bending by the punch in the early stages of the draw. The autographic record is affected in that the punch load falls to zero immediately upon fracture, the maximum value of P before fracture being taken as the apparent deep-drawing strength P_z. This is justifiable, provided the cup fractures after the flat peak of the pressure curve has been reached, otherwise a fictitious value is assumed, since the curve of punch load is still rising. Here the cup is only in the early stages of the draw before the side cylindrical wall commences to form. The author quotes results for iron (see Table I) and for aluminium with punch radii from 0·5 mm. to 9·0 mm. The results indicated that the punch radius should not be less than one-sixth the punch diameter for both iron and aluminium and not

greater than one-third for the latter, in order to maintain the maximum strength of draw.

LIMIT OF DRAWING AND COMPARISON OF MATERIALS

The ratio of the punch diameter to the blank diameter may be termed the drawing coefficient. The coefficient for the maximum size blank which can be drawn under a given set of conditions is the limiting drawing coefficient. This should be affected by the die radius and the range $r_d = 3 \cdot 0$ mm. to 12 mm. was investigated for iron and aluminium. The limiting coefficient decreases linearly with r_d, *i.e.*, D_o increases, the steel being slightly better throughout than the aluminium, thus for $r_d = 3$ mm. $D_o = 39$ mm. for iron and 38 mm. for aluminium. Provided a material is held under conditions of limiting holding force, this method of comparison gives a satisfactory comparative test.

DRAWING BY CONICAL DIE

The effect of employing a conical die of half-angle θ to the axis of the punch was investigated for values of θ between 30 deg. and 90 deg. The limiting holding force became zero for θ less than 60 deg., the holding pad being removed. The punch load decreased linearly with θ. Limiting drawing coefficients also decreased with θ and it was found that the aluminium for $\theta = 30$ deg. was now slightly better than the steel drawing a blank 44 mm. diameter as against 42 mm. for steel.

SURFACE AND THICKNESS STRAINS DURING PRESSING

The residual stresses and final strains in the pressed cup are of a complex nature and it is necessary to have some knowledge of their magnitude in order to give an approximate heat treatment prior to re-drawing. The strains are a function of the blank radius, so that the author engraved on the blank surface two mutually perpendicular diameters, with scale marks corresponding to internal diameters of 12 mm. and each additional 2 mm. The changes in dimensions could be accurately measured after drawing. The three principal strains are (*a*) changes in thickness, (*b*) hoop or circumferential strain, measured by the change in diameter of the rings, and (*c*) the radial strain, measured by changes in width between scale marks. Provided the specific gravity of the material does not change on cold working, the following relation holds :—

$$(1+e_t)\,(1+e_r)\,(1+e_d)=1,$$

where e_t is the circumferential strain and is the change in diameter divided by the initial diameter ; e_r the radial strain and e_d the normal strain or thickness change. Fig. 6 gives the distribution of these strains over the measured cup, the positive sign meaning tension or thickening and the negative sign compression or thinning.

The drawing conditions here were $t_o = 0 \cdot 492$ mm., $D_o = 35$ mm., $r_p = 2 \cdot 5$ mm., $r_d = 3$ mm., $d_1 = 18$ mm., and $d_2 = 19 \cdot 5$ mm. The thinning over the radius of the cup is 18 per cent., whilst the walls thicken $46 \cdot 4$ per cent. at the top. The hoop strain is seen to be compressive along the wall, increasing from zero at the radius to about 45 per cent. at the rim. The radial strain is tensile throughout.

The punch radius was expected to have considerable effect upon the thinning at the radius, since the larger radii would allow the metal to flow more easily to the regions where thinning is most likely to be predominant and the metal thickness would thereby be preserved. It was also felt that thinning would increase with the blank diameter, and therefore with the maximum punch load. The maximum thinning was found to decrease parabolically with increase of punch radius and to increase linearly with the blank diameter. Maximum thinning always occurs in the region about the radius of the cup, where the radial strain is large and is accompanied by little compressive strain. It is here, therefore, that failure is most likely to occur.

REDRAWING

In addition the author made a number of experiments with two-stage pressings. The maximum punch load (P_{max}) required to complete a successful draw was not dependent on the initial depth of cup, the autographic diagram revealing that the peak on the pressure curve is maintained over a longer period as

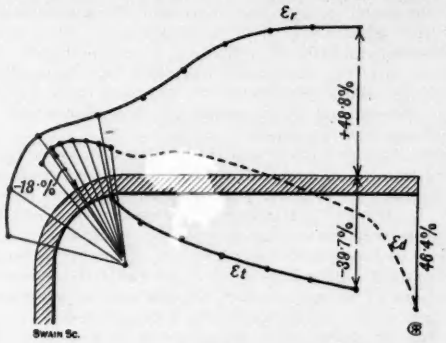


FIG. 6—*Distribution of Normal and Surface Strains for Iron Under Rigid Holding*

the depth increases. P_{max}, however, increased linearly with the severity of redrawing, *i.e.*, as the diameter of punch decreased for constant initial cup diameter. It should be noted that in redrawing the tendency to wrinkle is retarded by the stiffness of the side cylindrical cup wall which had thickened in the first stage.

REMARKS

Comparative results as to the relative ability of metals to draw are somewhat difficult to state, since the form of pressing and the conditions and type of straining vary so much in commercial practice that it is unlikely that comparisons made under one set of conditions will hold for other dissimilar conditions. Indeed, the experience of manufacturers has proved that certain materials are suited for certain jobs and are unsuited to others. In this light, therefore, researches such as this, which seek to determine the mechanism of the deep-drawing process and the effect of variables upon the types of strains induced, are valuable in that they enable results to be interpreted with some measure of confidence. It is to be regretted, however, that the work was not done for a larger size of pressing, so as to reduce the effects of minute inequalities to a minimum and possibly to bring out small tendencies which are otherwise masked when measurement is small dimensionally.

Properties of Thin Metal Films

No. I

THE investigation of the properties of very thin metallic films is of major importance in both physics and metallurgy. The mode of examination employed

is necessarily largely physical in nature, but any developments cannot fail to have the most valuable repercussions on metallurgical science. The whole subject is of great interest theoretically and also from a purely practical standpoint, owing to the growing use of surface films on metals. The best thin films are produced either by deposition from the vapour phase or by cathode sputtering. Many theories have been put forward for their remarkable behaviour, but they do not explain all the facts, and the anomalies observed apparently depend on several factors. Much has been done to determine the effect of these factors singly, but the problem is by no means solved. Metallurgically, the subject is also of special interest, since it affords the possibility of examining a whole series of metals in an amorphous condition. Where such layers play an important *rôle*, a knowledge of their structure is of prime importance. It is only necessary to refer to reflecting layers of metal on glass, their use in rectifiers, photo-cells, condensers, and high-ohmic resistances, to protective metal layers of all kinds, and those used in the important field of heterogeneous catalysis.

An extensive account of the structure and electrical conductivity of very thin metal layers, with numerous references to original publications, has been given by L. Riedel.[1] Although an attempt is made to discuss important recent work, a complete treatment of the whole subject is not claimed. A large amount of matter is, however, collected in the separate sections of the paper, each dealing with a particular aspect of the subject.

Suitable thin metal films cannot be produced by mechanical methods like rolling or beating, which cause irregularities, and also set a limit on the thinness attainable. Again, thin layers produced by chemical electro-deposition are generally unsuited for the investigation of physical properties, since they become contaminated by impurities which affect them in a quite uncontrollable manner. In consequence, the metallic films used for experimental purposes are almost always prepared by thermal condensation from the vapour phase, or by sputtering of the massive metal on to a " base " which is smooth, amorphous, and generally cooled.

The production of the film is by no means easy, as the smallest impurity introduced affects the electrical conductivity of the layers, and therefore a very high vacuum or a very pure " filler " gas (mostly of the inert variety) was found necessary. Only very clean apparatus must be used. The nature of the base on which the metal is to be deposited is also of great importance, and a special technique is adopted to get it ready beforehand. The speed of vaporisation must not be too high or the deposits become overheated, resulting possibly in a change in the structure of the layer. Again, special devices are necessary to control the amount deposited. Suitable bases on which to deposit are resistance glass and amorphous quartz, celluloid, and collodion skins, especially where it is desired to make optical measurements, and for special investigations on structure use is often made of the cleavage surfaces of crystals, such as rock salt, &c. When resistance measurements are to be made, suitable contacts for introducing the current are obtained by electrolytically depositing thick strips of silver or copper.

MEASUREMENTS OF THICKNESS

The thickness of these very thin layers must be accurately determined. Most methods rely on calculation, since the total weight and the specific gravity of the deposited metal are known, and the area it covers can be accurately measured. Another way is to dissolve off the deposit chemically and determine the metal quantitatively. An elegant method depends on the quantitative emission of ions at high temperature when a piece of specially prepared tungsten is placed in the stream of metal ions. Most of these methods assume that the specific gravity of the metal in the thin layer is equal to that of the same metal when in the normal massive form. To find if this is so, it is necessary to determine the actual thickness of the layer, and a fairly accurate method (though only suitable for relatively thick layers) depends on the observation of Newton's rings. Polarisation measurements enable the thickness of silver layers between 5 and 25 mμ to be fairly accurately determined.* The thickness of nickel layers deposited from the vaporised condition was calculated from interference phenomena during reflection of Röntgen rays from the front and back of the layer itself. It was found that a reduction of 15 to 20 per cent. occurred in the specific gravity of metal deposited under high-vacuum conditions as compared with the normal values. This applied only to layers less than 180 mμ thick, and its cause was traced partly to an enlargement of the nickel space lattice brought about by the presence of absorbed gases. This change in the lattice size amounts to 4 per cent. In the case of silver and gold films, the lattice constants increased about 1 per cent., and the same was found for indium. However, the reduction in the specific gravity of the nickel seems exceptional, since it possesses a specially strong tendency to absorb gases, like palladium which stands in the same group of the periodic table. Indeed, it was found with sputtered films of nickel that at least four different structures are obtainable, depending on the nature of the " filler " gas used. Small quantities of hydrogen also play a specially important *rôle*.

Different methods used to determine the thickness of silver films give rise to the probability that the specific gravity of the metal in layers about 15 mμ thick is the same as for the massive form. It is quite impossible to determine the thickness by the electrical resistance method, since the resistance depends so very much on the structure of the layer, which is unknown, as well as on its actual thickness. It is found, however, that the optical constants for silver layers above about 30 mμ thick are similar to those for the metal in the massive form. The optical method is relatively simple to apply, and is also useful for testing the uniformity of the films.

CONDUCTIVITY OF METALLIC FILMS

Measurements of the resistance (at constant temperature) of layers produced as described above often disclose a spontaneous and irreversible fall in resistance, which is most marked just after deposition of the layer. A strong increase, depending on the time subsequent to deposition, is found in some instances. The reduction in resistance is much accelerated, and the end value much reduced, by raising the temperature. This irreversible increase in conductivity may be very large. In any explanation of the phenomenon ageing effects and changes in internal structure of the films are necessary assumptions. Deposits produced at low temperatures have a colloidal or possibly even an amorphous structure, but it is found that, spontaneously or on heating, they more or less completely assume a normal crystalline condition, a change which may probably be connected

* 1 μ=1 micron=one thousandth millimetre ; 1 mμ=one millionth millimetre.

with a degassing action. This process is naturally accompanied by a strong increase in the conducting power of the metal and the anomalous temperature coefficients obtained tend towards the values characteristic of the metal in the massive form. Below a thickness of 30 mμ and after ageing, the specific resistance increases with decreasing thickness of the layer, at first slowly, but at a "critical" thickness of approximately 1 to 10 mμ extremely rapidly. In films a little thinner, it is so big as to be not easily measurable. This is explainable by Thomson's theory of the shortening of the mean free path of the electrons in the case of very thin layers, which, however, does not explain the big increase at certain "critical" thicknesses, and resort is then made to Swann's grain theory which has received ample experimental verification. It has also been suggested that a non-conducting metallic surface layer exists on the outside of the layer itself.

The resistance of a 115 mμ thick copper foil, freshly prepared, remains constant with time when measured at 20 deg. abs., but if heated to 80 deg. abs. a marked and irreversible reduction of resistance occurs. If cooled back to 20 deg. abs., there is a reversible reduction in resistance, though the temperature coefficient is twenty times smaller than for the same metal when in the massive form. This effect is repeated when the temperature is again raised. The spontaneous change of the resistance with time at constant temperature seems to be very small. The same is found for layers of silver, gold, and cadmium about 100 mμ thick. These irreversible changes are doubtlessly due to the highly "disordered" state at low temperatures of the structure of the condensed layers. Thus on heating, the vibrations of the atoms increase and they are then able to swing over and take up more and more the normal crystal lattice structure. The first atoms to reach the normal position are those only very slightly displaced, whereas still more heating is required to ensure return of those atoms displaced to a greater extent. Accordingly there exists a definite state of "order" at each temperature, and hence a definite resistance, too. Layers of certain metals will be more "ordered" than others. Those with a low characteristic temperature, which is inversely proportional to the amplitude of the atomic vibrations, occur in an "ordered" condition, compared with layers composed of metal having a higher characteristic temperature. This is confirmed for layers of lead and thallium, where the electrical conductivity on heating to room temperature comes very near to that of the metal in the massive form. An irreversible increase in resistance is found on heating bismuth, which agrees with the abnormal increase on passing from the molten to the crystalline condition and is traceable to a decrease in the number of electrons brought about by the reduced reciprocal action of the atoms (volume increase on crystallisation). Bismuth films are also found to have a negative temperature coefficient, and on cooling of the layer the resistance increases reversibly. Suhrmann and Barth[3] attribute this to the abnormally long free path of the conducting electrons. Such changes from a "disordered" to a crystalline condition are confirmed by determinations of the reflecting power of these layers during ageing.

TRANSFORMATION FROM AMORPHOUS TO CRYSTALLINE STRUCTURE

Important experiments were carried out by Kramer,[3] who found with relatively thick layers (about 100 mμ) that the conductivity of the deposits first remains almost constant during heating and then rises suddenly to a considerable value in a very narrow temperature interval, finally approaching more and more the value for the normal crystalline metal. The layers employed were too thick to show any marked anomalies, but the high initial resistance points to the existence of a greatly distorted lattice. With sufficiently slow heating the sudden reduction in resistance may be well reproduced, so Kramer maintains that this transformation temperature (designated T_u) can be given accurately to within 5 to 10 deg. and is characteristic for the metal. Values determined for T_u are given in the following table :—

Metal.	T_u° abs.	Metal.	T_u° abs.
Zn	130	Sb	446
Cd	150	Mo	210
Hg	160	Fe	440
Al	140	Ni	336
Sn	180	Pt	510
Pb	455	Ir	275

For very thin layers the idea of a transformation temperature as a constant of the material loses its significance. The above values refer solely to the change of the compact metal from the "amorphous" to the crystalline condition. T_u may be calculated from the electrical conductivity of the metal when in the massive form from the equation

$$\sigma = \frac{C\,N^{2/3}}{T_u V_a^{2/3}} \text{ (Kramer)},$$

where σ is the electrical conductivity of the metal at 0 deg. Cent., V_a the atomic volume, N the number of free electrons per atom (a small whole number for good conductors), and T_u the measured transformation temperature. A good approximation to a constant value is always obtained for C. A comparison of this empirical relation with Sommerfeld's conductivity formula indicates that the transformation temperature should be inversely proportional to the mean free path of the electrons in the metal, when in the massive form, a result which Kramer finds to be very plausible. The relationship shows that metals with a greater thermal mobility possess a higher transformation temperature. In the case of very thin layers of metal produced by the vaporising process a sharp discontinuity may occur in the irreversible resistance-temperature curve ; with increasing thickness the discontinuity becomes distinctly flatter and becomes displaced to lower temperatures. The following recrystallisation temperatures were calculated by Fukuroi[4] from an empirical relationship connecting the thickness of the layer and the temperature at which the big rise in conductivity sets in :—Zinc, 277 deg.; cadmium, 241 deg.; antimony, 337 deg.; magnesium, 330 deg. abs. Kramer obtains different values, but there is some proportionality to the melting point of the respective metals.

It is also remarkable that ferro-magnetism in the crystal structure of iron and nickel layers appears pretty suddenly on heating above the transformation temperature according to the electrical conductivity measurements. An "agglomeration" hypothesis seems the most likely explanation at present of the anomalies in the conductivity of metal deposited from its vapour.

SPECIFIC RESISTANCE AND THICKNESS

The mean free path of the electrons within the metal can be determined with some certainty from the dependence of the specific resistance of thin metal wires on their diameters, especially at low tempera-

tures. Such experiments are not easy, but the remarkably surprising result is obtained that the free-path length of the electrons is extremely large for relatively thick platinum wires such as exceed 15 μ. At 0 deg. Cent. the value is 3·7 μ, which is seventy times as great as for silver and 600 times as great as for lead. A wire 0·2 mm. thick, at the melting point of ice, has a specific resistance some 1·5 per cent. larger than for the metal in the massive form as a result of the decreased free-path length. The conductivity was reduced by about 6 per cent. at 0 deg. Cent. in the case of platinum wires 0·05 mm. thick, such as are frequently used for resistance thermometry, and it seems astonishing that this big effect was not discovered empirically long ago. For investigations of this kind metal layers, however, possess definite advantages over the employment of wires. The production of the layers and their contacts for

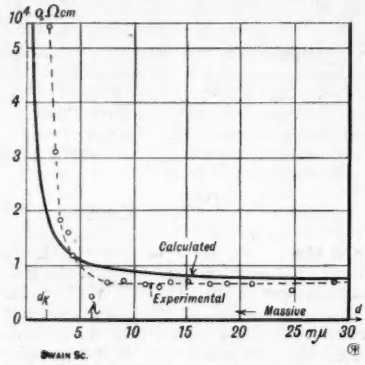


FIG. 1—*The Relation Between the Specific Resistance of Platinum and the Thickness of the Layer. (Patterson)*

joining the conducting wires are relatively simple, and layers of any desired thinness can be made and so very big effects can be obtained. Film thicknesses are easily determined and all metals may be made use of.

It was shown by J. J. Thomson a long time ago that, if the mean free path length of the electrons is of the same order of magnitude as the thickness of the layer of metal, the specific resistance could not be regarded as a constant of the material. This is attributed to the impingement of the electrons on the two outside surfaces of the layer, as a result of which there is a reduction in the length of the mean free path with consequent fall of the electrical conductivity. If d is the thickness of the layer and λ the mean free path of an electron in the massive metal, the theoretical increase of specific resistance with diminishing film thickness is indicated by the following figures:—

For d/λ	4	... 1	... 0·1	... 0·01
Relative increase in specific resistance	1·07	... 1·33	... 7·13	... 32·0

The specific resistance of platinum and its dependence on the thickness of the layer was investigated by Patterson,[5] and he obtained results which have been amply confirmed, and which are extremely characteristic. The layers were produced by sputtering, and aged at 110 deg. Cent. It is found for a thickness above 20 mμ that the specific resistance is practically constant, but considerably higher generally than for the crystalline metal in the massive form. The results are shown graphically in Fig. 1, in which one of the curves has been plotted from calculated data, and the other plotted from data obtained experimentally. The unbroken curve represents the former, and was calculated from Thomson's equations and available data. The curves give $0·75 \times 10^{-4}$ ohm-centimetre as a limiting value at 30 mμ, compared with $0·105 \times 10^{-4}$ for platinum when in the massive form. Now below a thickness of 20 mμ the resistance rises slowly and then finishes up very steeply. Further, it approaches an infinite value for a certain finite value of the thickness, designated d_k, which various investigators have found to be nearly 2 mμ. This limiting or "critical" thickness for platinum affords a very interesting comparison with that obtained for other metals, for which it is mostly higher. Thus for silver it is about 5, for gold 3, and for nickel 12 mμ, whilst for iridium and tungsten smaller values are obtained of 0·4 and 0·2 mμ respectively. Fig. 1 certainly shows that the specific resistance is many times higher than for the normal crystalline metal. For the thicker layers the measured values show remarkably good agreement with Thomson's theory, but for very small thicknesses there is a marked deviation of the experimental from the calculated curve. Formulæ may, however, be fitted to the experimental curves for the purpose of estimating the mean free path of the electrons.

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[2] *Z. Physik*, 1936, 103, 133.
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(*To be continued*)

Books and Publications

Metallurgy for Engineers. By E. C. ROLLASON. 8vo, pp. viii+272. 1939. London: Edward Arnold and Co. 10s.

THE rapid advance of metallurgical practice has made an increasingly wide range of materials available to engineers, and it is evidently desirable (as recognised by the examinations of universities and engineering institutions) that they should be familiar with the metallurgical principles which will enable them to make the best choice of the existing materials. Hence metallurgical text books, written with the special intention of aiding the engineering student, are to be welcomed. In this book Mr. Rollason has provided an account of metallurgical theory and practice which adequately covers the information necessary for the appreciation of metallic materials of construction, ferrous and non-ferrous. It includes a description of mechanical testing, macro- and micro-examination, and a discussion of solidification phenomena, equilibrium diagrams, mechanical deformation and annealing which illustrate principles common to all metals. The specific materials are then dealt with in more detail—iron and steel, alloy steels, cast iron, copper alloys, and light alloys. There is additional information on the metallurgical changes which accompany welding operations. A number of clearly drawn diagrams aid considerably in emphasising important features in structure, design, and procedure. The book is written in a concise and interesting manner and may be recommended to engineering students, and, as an introductory course, to students of metallurgy. Engineering inspectors, who are too often preoccupied with mechanical testing, also will find it a refreshing and profitable study of the origin and characteristics of the materials with which they have to deal.